Strong Velocity Effects in Collisions of He$^+$ with Fullerenes

T. Schlathölter, O. Hadjar, R. Hoekstra, and R. Morgenstern

KVI Atomic Physics, Rijksuniversiteit Groningen, Zernikelaan 25, 9747AA Groningen, The Netherlands
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We have studied fragmentation and ionization of C_{60} by He$^+$ impact over a velocity range from 0.1 to 1 a.u. where a transition from vibrational to electronic excitation is predicted. With increasing velocity we observe a strong decrease of evaporative processes (C_{60-2m}^{r+} peaks) and a linearly increasing yield of small fragments (C_n^+, $n < 15$). Apparently direct vibrational excitation leads preferentially to evaporation, whereas electronic excitation is responsible for multifragmentation. In the intermediate range we find indications for a "transparency window" similar to that predicted recently in simulations of Na$_9^+$-He collisions. [S0031-9007(98)08105-8]

The interaction of fullerenes with particles such as photons [1], electrons [2], and ions [3] leads to fragmentation patterns which can serve as a fingerprint of the interaction process. Ion-fullerene (and fullerene-ion-atom) collisions have been studied for different collision systems at a variety of collision velocities and projectile charge states recently. In the $E_{c.m.} < 250$ eV range (corresponding to a projectile velocity of ≈ 0.05 a.u.; in the following, we will always use the projectile velocity to characterize the collision), collisional fragmentation is mainly due to direct vibrational excitation of the target clusters [4]; the bimodal fragment distributions show close similarities to, e.g., photofragmentation results [1], indicating an independence of the fragmentation process on the exact nature of the excitation mechanism [5]. Little is known about the excitation mechanisms in the keV range ($v \approx 0.1-1$ a.u.), where the interaction times are much shorter. In this range, collisions of multiply charged ions with fullerenes have been studied with great interest [6–9]. These collisions lead to remarkable mass distributions of the collision products. On the one hand, C_{60}^{r+} clusters are formed in a gentle way [10,11], for highly charged projectiles up to $r = 9$ [12]. On the other hand, the fragment distribution (C_n^+) peaks at $n = 1$, i.e., very small fragments are formed in such collisions. Similar results are observed for MeV collisions ($v > 1$ a.u.) of multiply charged ions with fullerenes [13–15]. Whereas the first finding can be explained by electron capture at large distances, without kinetic energy transfer from the projectile to the C_{60}, the explanation for the occurrence of the small fragments is less obvious. Under the assumption that these fragments are due to very close collisions, one can obtain information about the mechanisms by varying the collision energy. Furthermore, a singly charged projectile is favorable for such a study to avoid potential energy effects.

We investigate the transition from vibrational to electronic excitation in such close collisions experimentally for the system He$^+$-C_{60} in the velocity range between 0.1 and 1 a.u.

For the present experiment He$^+$ ions are extracted from an electron cyclotron resonance source, floated on a potential between 1 and 28 kV. A double gap linear accelerator operated at 13.56 MHz is used to increase the projectile energy up to 105 keV. In the collision chamber a fullerene oven is operating at about 700 K. The C_{60} vapor effuses through a nozzle into the collision region where it is crossed by the projectile ion beam.

Because of a static electric field (250 V/cm) all charged collision products are extracted from this region. A reflection-type time-of-flight (TOF) mass spectrometer [16] (resolution ≈ 430) is used to determine the charge-to-mass ratio of the fragment ions. The fragments can be detected in coincidence either with an electron emitted during the collision or with charge state resolved projectiles, which serve as the start signal for the TOF measurement, respectively. Alternatively, the projectile beam can be chopped, with the chopper pulse being the start signal. For the present study the latter method is used, in order to collect the collision products independent of the nature of the collision process. Details of the experimental setup can be found in [17].

Typical n/r spectra (Fig. 1, with n being the number of C atoms and r the charge state) for He$^+$ collisions with C_{60} show that C_{60}^{r+} is formed up to $r = 3$ and with a lower extraction voltage even C_{60}^{4+} can clearly be identified. Furthermore, the presence of C_{60-2m}^{r+} peaks indicates evaporative cooling (e.g., $C_{60}^{r+} \rightarrow C_{58}^{r+} + C_2$, $r = 1-3$) and superasymmetric fission (e.g., $C_{60}^{r+} \rightarrow C_{58}^{(r-1)+} + C_2^+$, $r \geq 3$). The latter is a two-step process consisting of evaporation followed by electron transfer. For $r \leq 2$ superasymmetric fission is endothermic and therefore unlikely to occur. Also for $r = 3$ evaporation is the dominant process [18]. Small carbon clusters (C_n^+) appearing over a wide mass range ($n \approx 1-15$) are therefore, in the first place, due to multifragmentation processes into rings ($n \geq 10$) and chains ($n \leq 10$).

With increasing projectile velocity, two opposite trends are observed: (i) the intensity of the multifragmentation peaks increases strongly, the maximum of their
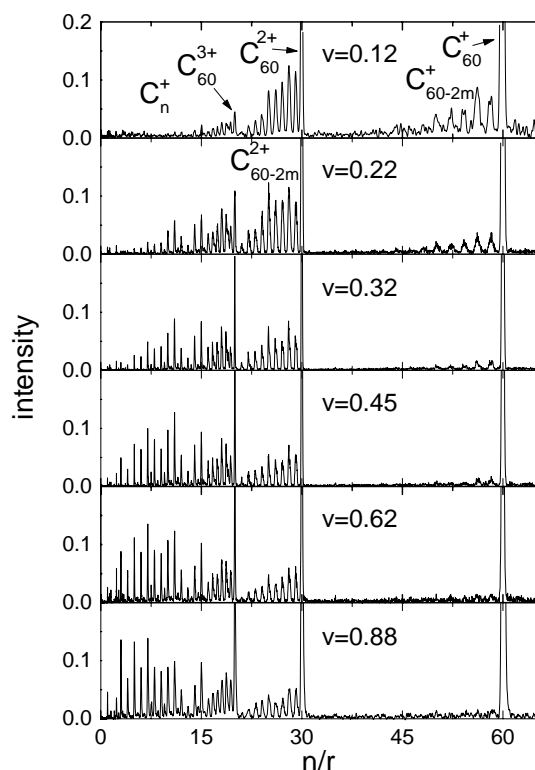
FIG. 1. Mass spectra of C_{60}^{r+} and fragment ions at different collision velocities v (in a.u.). The C_{60}^+ yield is normalized to 1 and the ordinate ranges from 0 to 0.2.

distribution shifts to smaller n values, and the yield of C_{60}^{2+} and C_{60}^{3+} increases; (ii) the intensity of the C_{60-2m}^{r+} ($r = 1, 2$) peaks decreases.

To model the direct vibrational excitation of the C_{60} due to the He$^+$ impact, we developed a molecular dynamics (MD) code, based on a realistic three-body potential for the fullerene [19] and a screened Coulomb potential for the He-C interaction, the latter with the screening function of Molière [20] and the screening length of Ehlich *et al.* [21]. This scheme has been successfully applied to low energy collisions of He with fullerenes ($v \leq 0.05$ a.u.) [22]. The quantity of interest for our study is the energy transfer from the projectile to the fullerene, to which we refer to as elastic (projectile) energy loss. This quantity is easily accessible from a MD simulation, since it can be obtained as soon as the projectile leaves the interaction region. If the resulting vibrational excitation of the fullerene exceeds the activation energy of the process $C_{60} \rightarrow C_{58}^+ + C_2$ evaporation occurs ($E_{act}^{exp} = 7.1$ eV [23], $E_{act}^{theor} \approx 12$ eV [24]). It is therefore possible to calculate the relative evaporation cross section as the ratio of the number of trajectories with above threshold elastic energy loss to the total number of trajectories.

To this end, He projectiles are launched with a certain velocity v at random (x, y) coordinates within an impact radius $R_1 = 11$ a.u. This R_1 is estimated with the classical over-barrier model which assumes that at a critical distance the potential barrier between projectile

and target is lowered below the target ionization potential such that a target electron can move to the projectile. $R_1 = 11$ a.u. corresponds to an electron capture cross section $\sigma = 1.06 \times 10^{-14}$ cm^2. For each trajectory, a random orientation of the fullerene is chosen. The highest elastic energy losses occur for collisions with the shell of the target ($b \approx 6.5$ a.u.), where the projectile experiences the highest density/cm^2 of C atoms. For smaller values of b, the average elastic energy loss decreases slowly, outside the cage it drops to zero very fast. By far the most trajectories lead to elastic energy losses of a few eV only.

The theoretical results can be compared directly to our experimental data. From the n/r spectra we can obtain the peak integrals for the different contributions. The relative cross section for evaporative fragmentation is defined as

$$\sigma_e = \frac{\sum_{m=1}^{9} \int C_{60-2m}^+}{\int C_{60}^+ + \sum_{m=1}^{9} \int C_{60-2m}^+} . \qquad (1)$$

Experimental data as well as MD results for both activation energies are shown in Fig. 2. Obviously, all curves have a $1/v$ dependence, i.e., the probability for evaporation scales linearly with the interaction time of projectile and fullerene. The MD calculations mimic the relevant process qualitatively correct, therefore the C_{60-2m}^+ can serve as a fingerprint for evaporation induced by direct vibrational excitation (EVE). (We note that a $\frac{1}{v}$ dependence is also found for evaporation from C_{60}^{2+}. It has to be kept in mind however that these ions can be formed only by a direct ionization, i.e., an electron excitation, leading to an offset on the relative yields. For C_{60-2m}^{2+} the elastic part cannot be separated.) The quantitative discrepancy between experiment and theory might be partly due to an overestimation of the electron capture radius but is mainly due to the fact that the C_{60}^+ yield in the experiment is reduced by electronically induced fragmentation and ionization processes. It has been shown recently that for ion-metal cluster collisions even at lower energies electronic excitations can be an important fragmentation channel [25].
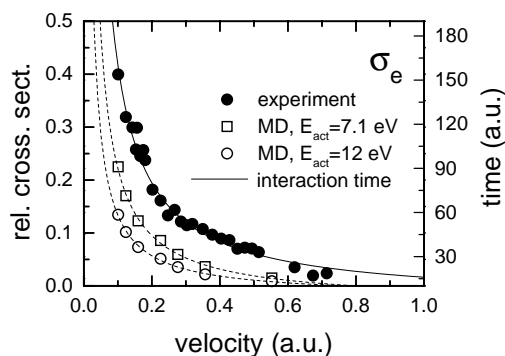

FIG. 2. Relative cross sections for evaporative fragmentation ($C_{60}^+ \rightarrow C_{60-2m}^+ + C_{2m}$); dotted lines: $1/v$ fit; solid line: interaction time for collisions with $b = 0$.

To model electronic excitations we treat the large number of valence electrons in the metal-like C_{60} as an electron gas. Inelastic energy loss of ions traveling through an electron gas is due to long range coupling to electron-hole pairs [26]. In the energy range under study, it scales linearly with the projectile velocity v and can thus be described by the stopping power $S = \frac{dE}{dR} = \gamma(r_s)v$ [27]. The friction coefficient γ depends on the density parameter $r_s = (\frac{4}{3}\pi n_0)^{-1/3}$ which is a function of the valence electron density n_0.

The valence electron density for a fullerene is assumed to be a spherically symmetric jellium shell as calculated by Puska and Nieminen [28]. With R being the distance from the fullerene center in atomic units, $n_0(R)$ decays outside the shell and towards the center in a way that the main contribution is found for $4 < R < 9$. The friction term γ for a variety of projectile ions and for different values for r_s can be found in [29]. It can be interpolated nicely by the exponential $\gamma(r_s) = 0.755 \exp(-\frac{r_s - 1.5}{0.88})$.

Embedding of the friction into the MD formalism leads to a scheme to obtain the inelastic energy loss: After each MD integration step, the projectile energy is reduced by

$$\Delta E = \gamma(r_s(R))v\Delta R = \gamma(r_s(R))v^2\Delta t. \quad (2)$$

The inelastic energy loss exceeds the elastic energy loss by far. A maximum is again found when the projectile impinges close to the fullerene shell (due to the long trajectory part through high density areas of the electron gas). Inside the shell, significantly less inelastic energy loss is observed. Outside the shell a fast decrease with the impact parameter is found. The regimes can even be recognized as three distinct peaks in the total energy loss histogram. The average inelastic energy loss ($\Delta E \approx 5.9v$) is close to the value obtained analytically for a He projectile, passing the fullerene target at $b = 0$ without deflection,

$$\Delta E = 2 \int_0^\infty \gamma(r_s(R))v\, dR \approx 8.1v. \quad (3)$$

This is in good agreement with experimental results for the inelastic energy loss of a He ion passing a graphite target of thickness 14 a.u. [30]. A first surprising result of the simulation is the fact that over the whole projectile velocity range under study a direct collision with the fullerene cage leads to an inelastic energy loss exceeding the evaporation threshold. From this one would expect the relative cross section for evaporation to increase with the projectile velocity. Since the opposite is observed, we conclude that electronic excitation leads to fundamentally different deexcitation processes, namely, multifragmentation. The fact that also the C_{60}^{r+} yields ($r > 1$) increase with v (Fig. 1) furthermore indicates an increasing importance of direct ionization.

This differs from the results of a recent theoretical study by Campbell et al. [5], where an independence of the fragmentation process from the excitation mechanism was found. Their results also predict a phase transition

from evaporation to multifragmentation for average internal fullerene energies between 80 and 225 eV, and the calculated fragmentation patterns are in agreement with experimental results obtained by fullerene-ion-atom collisions ($v < 0.55$ a.u.) and multiphoton ionization. We observe a coexistence of evaporation and multifragmentation over the whole excitation energy range under investigation (15–165 eV; see Fig. 3a), i.e., no indication of a phase transition (for projectile velocities v below 0.22 a.u., even the maximum loss is below 80 eV).

The activation energies for multifragmentation and direct ionization are not known, and furthermore the employed stopping power model does not account for the statistical nature of the inelastic processes. Therefore we cannot calculate the relative fragmentation cross sections and in the following we will compare the average inelastic energy loss to the experimental results on adjusted scales.

To this end the (experimental) relative cross sections for multifragmentation σ_f and collisional ionization σ_i are defined

$$\sigma_f = \frac{\sum_{n=1}^{14} \int C_n^+}{\int C_{60}^+ + \sum_{n=1}^{14} \int C_n^+}, \qquad \sigma_i = \frac{\int C_{60}^{r+}}{\int C_{60}^+ + \int C_{60}^{r+}},$$
$$r = 2, 3. \quad (4)$$

Results from experiment and simulation are shown in Figs. 3a and 3b. Apparently, a threshold for multifragmentation of C_{60} by He^+ impact exists at $v \approx 0.1$ a.u. from which it increases linearly up to $v \approx 0.6$ a.u. From
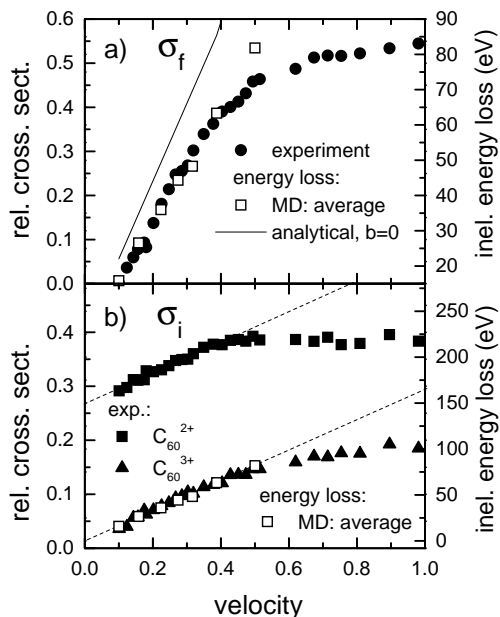

FIG. 3. Relative experimental cross sections for multifragmentation (a) and C_{60}^{r+} formation (b) (closed symbols and left axis) and calculated inelastic energy loss (open squares, solid line and right axis). The scales have been adjusted to show that the experimental data exhibit the same linear dependence on the collision velocity as the calculated inelastic energy loss. The dashed lines in (b) are to guide the eye, their slope follows the trend of the inelastic energy loss.

the linearity of experimental and simulative data we conclude the multifragmentation to be due to inelastic energy loss processes. In the following, we call this process fragmentation by electronic excitation (FEE). The direct ionization also scales linear as the FEE up to $v \approx 0.5$ a.u. ($r = 2$). For $r = 3$ deviations from the linear scale can be seen, which might be due to the decreased stability of C_{60}^{3+} compared to the lower charge states. The deviation of the FEE related quantities from the linear scale for velocities larger than 0.5 a.u. can be due to additional mechanisms which become important at higher energies, e.g., plasmon excitation.

In a recent nonadiabatic quantum molecular dynamics study of Na_9^+-He collisions, Saalmann et al. predicted a transition from direct kinetic energy transfer in the low velocity range to electronic excitation for higher velocities [31] which even leads to a transparency of the cluster in the transition region, where both contributions are weak. The $1/v$ dependence of the EVE process and the linear v dependence of the FEE process lead to a similar behavior, indicating the existence of such a transparency window for ion-fullerene collisions. It reflects the well-known velocity dependence of nuclear and electronic components of the stopping power [32].

In conclusion, two different processes (FEE and EVE) could be identified as being active in fullerene fragmentation by ion impact in the velocity range 0.1 a.u. $< v <$ 1 a.u. The fragmentation pattern depends strongly on the nature of the excitation, in contrast to findings for collisions at lower velocities. Strong indications for the existence of a "transparency window" in ion fullerene collisions could be found.

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